EPITAXIAL GROWTH OF Pt(001) THIN FILMS ON MgO(001) UNDER OXIDIZING CONDITIONS

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ABSTRACT

Epitaxial Pt(001) thin films have been grown on MgO(001) substrates using dc magnetron sputtering with an Ar/O_2 mixture at 700°C. The width (FWHM) of the rocking curve of the Pt(002) peak is between 0.16° and 0.20°, which is only 0.05° wider than that of the MgO (002) peak of the cleaved substrate. The film surface roughness is about 1 nm (rms) for a 240 nm thick Pt film. No grain structure could be observed using SEM. In contrast, the films deposited at 700 °C with pure Ar, have both Pt(111) and Pt(001) oriented growth, as shown by XRD $\Theta - 2\Theta$ scans, with the Pt(111) peak having the largest intensity. $BaTiO_3$ epitaxial films have also been deposited on Pt(001)/MgO(001). The width (FWHM) of the rocking curve of the $BaTiO_3$(200) peak is 0.4°. The surface morphology of the epitaxial $BaTiO_3$(100) thin films on Pt(001)/MgO(001) is featureless. XRD pole figure measurements on $Pt/BaTiO_3/Pt$ trilayer shown a very good in-plane alignment of all layers. The epitaxial growth relationship was also confirmed by TEM electron diffraction and cross-section imaging. The $Pt/BaTiO_3/Pt$ epitaxial trilayer could serve as a prototype for ferroelectric capacitors and may be able to improve the electrical properties of the capacitors.

INTRODUCTION

In multilayer systems, epitaxial growth has been an important issue for high quality multilayer structures and of great interest for applications. Epitaxial growth of metallic films is also important in oxidizing environments employed in the deposition of ferroelectric, magnetic oxides and HTSC films. Recently, Lairson et al. [1] reported epitaxial growth of Pt films on MgO(001), MgO(110), MgO(111), and Al_2O_3(0001) substrates using a sputtering technique. In a pure argon atmosphere of 3.0 mTorr, the relative intensity of Pt(111) to the total Pt(111) and Pt(200) peak intensity varied from nearly 100% for temperatures below 550°C to 0.1% at a deposition temperature of 680°C when MgO(001) substrates were used. In a mixture of 10 mTorr Ar and 5 mTorr oxygen, epitaxial growth of Pt(001) on MgO(001) at 680°C was demonstrated. In this report, we present data showing the epitaxial growth of Pt(001) on MgO(001) at 700°C with a mixture of 6 mTorr Ar and 5 mTorr O_2 . Pt(111) and Pt(200) oriented growth was observed when Pt was deposited in pure Ar at the same temperature. The epitaxial Pt(001) films grown under oxidizing conditions have mirror-like surfaces with a surface roughness of 1 nm (rms), single crystal-like structure and rocking curve widths as low as 0.2°. These films have been shown to be suitable for subsequent growth of epitaxial films and multilayers of ferroelectric materials.

DEPOSITION PROCESS

A vacuum chamber was equipped with a 2" magnetron sputtering gun which can be operated in a dc or rf mode, and with a 2" resistance heater (US

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GUN II). A turbo pump was used to reach a base pressure of 1-3 x 10^{-6} Torr. A Pt metal target was used with a purity of 99.95%. Ultra high purity oxygen gas (minimum purity 99.99%) and zero grade argon gas (THC less than 0.5 ppm) were used as working gases. The distance between the target and substrates was 10 cm. MgO substrates were used in this work. The substrates were cleaned with dichloromethane (methylene chloride CH_2Cl_2), acetone and methanol in an ultrasonic bath, then blown dry with nitrogen before loading into the chamber.

The experimental parameters used are shown in table I.

Table I Experimental parameters

Run	Samp.	Substrate	Ts °C	Ar/O2 mTorr	Thick nm	Orientation Pt(###)	FWHM ω
I	PT03A	MgO(100)	695	4.2/0	100	(111)+(200)	0.33°/0.7°
	PT03B	MgO(100)	695	4.2/0	100	(111)+(200)	0.33°/0.63°
II	PT04A	MgO(100)	695	6.4/4.6	170	(200)	0.23°
III	PT05A	MgO(100)	700	5.6/4.8	240	(200)	0.20°
	PT05B	MgO(100)	700	5.6/4.8	240	(200)	0.18°
	PT05C	MgO(100)	700	5.6/4.8	240	(200)	0.16°
	PT05D	MgO(100)	700	5.6/4.8	240	(200)	0.18°

CRYSTAL STRUCTURES

A Rigaku VS - DXR3000 diffractometer was used for the film structure characterization. Cu K_α monochromatic radiation was used in these experiments with a graphite 224R monochrometer to avoid any K_β line from appearing the diffraction patterns. The instrumental resolution for the rocking curve is 0.08°. A pole figure camera was used to determine the quality of the in-plane alignment between the film and substrate and between multilayers.

A typical $\Theta - 2\Theta$ Scan of an epitaxial Pt(001) film on MgO(001) is shown in Fig. 1a. Only the MgO(002), Pt(002), MgO(004) and Pt(004) peaks could be observed.

Expanding the intensity scale by 1000x as shown in Fig. 1b did not reveal any additional features. The rocking curve width (HWFM) is 0.20° for Pt(002) and 0.15° for MgO(002) as shown in Fig. 1c. These data indicate the epitaxial growth of Pt(001) on MgO(001), which was reproducible.

In contrast to the oxidizing sputtering condition, Pt(111)/Pt(002) oriented growth on MgO(001) substrates was observed at the same substrate temperature when sputtered in pure Ar. Surprisingly, no Pt(220), Pt(311) peaks appeared in the XRD at 2Θ=67.5° and 81.3°, respectively. The rocking curve width (FWHM)

was 0.33° for Pt(111) and 0.7° for Pt(002) as shown in Fig. 2c.

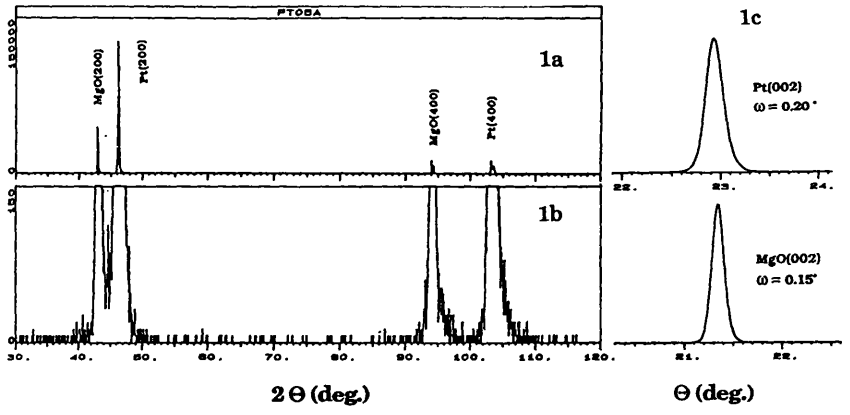

Fig. 1a and 1b A typical $\Theta - 2\Theta$ Scan of epitaxial Pt(001) film on MgO(100).
1c Rocking curve of Pt(002) peak and MgO(002) peak.

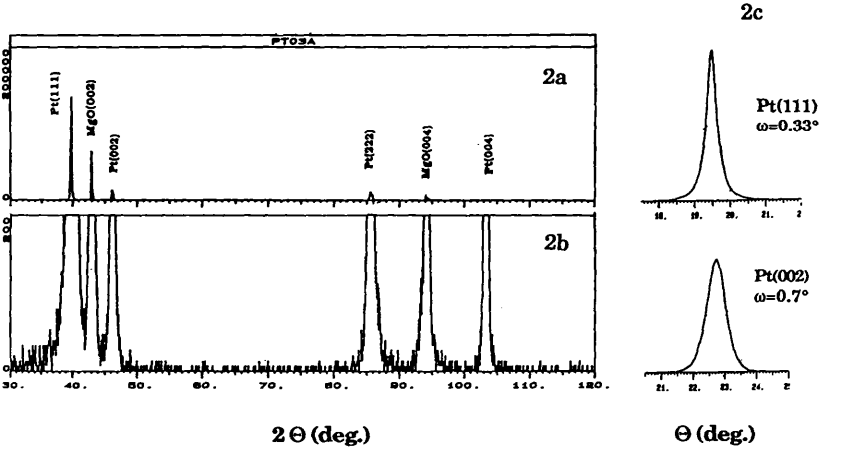

Fig. 2a and 2b A $\Theta - 2\Theta$ Scan of Pt(111)/Pt(002) oriented growth on MgO(100).
2c Rocking curve of Pt(111) peak and Pt(002) peak.

Pole figure measurements of a trilayer sample of $Pt/BaTiO_3/Pt/MgO$ are shown in Fig. 3. A schematic cross-section view of the trilayer is shown in Fig. 3d. The x-ray measurement probes all three films, so that the in-plane orientation of each can be determined. The MgO(202) peak was chosen for MgO substrate pole figure measurement as shown in Fig. 3a. The intensity of MgO(202) was not very strong because of attenuation due to the trilayer of

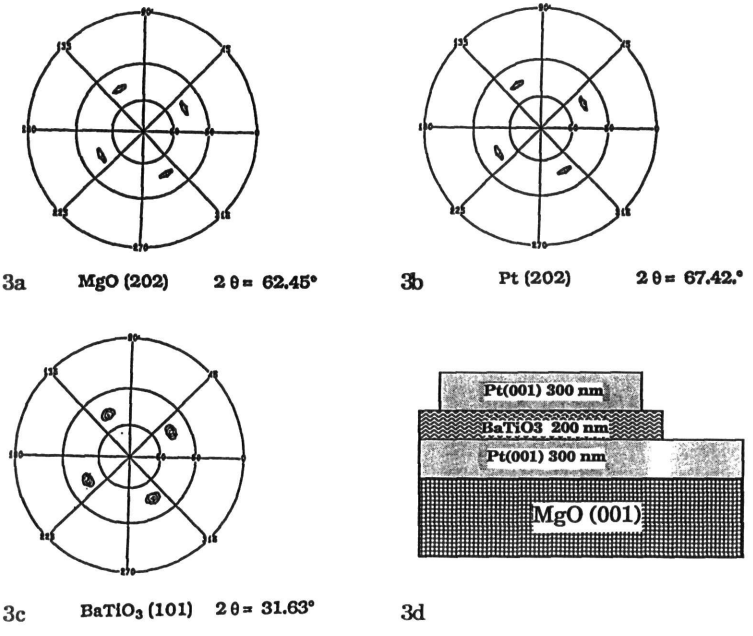

Fig. 3 Pole figure measurement on Pt(001)/$BaTiO_3$(001)/Pt (001) trilayer

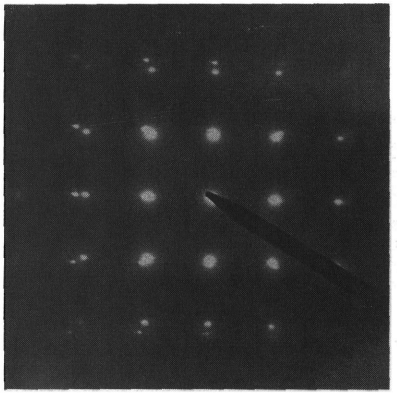

Fig. 4 Electron diffraction pattern of the epitaxial Pt film on MgO substrate. It indicates Pt[001] // MgO[001] and Pt[100] // MgO [100].

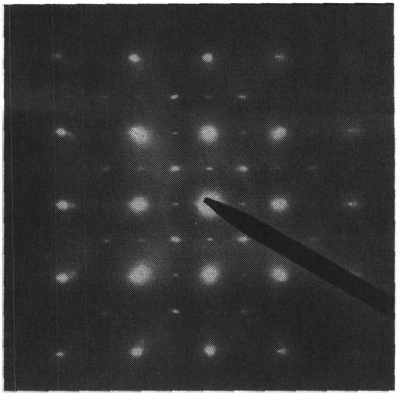

Fig. 5 Electron diffraction pattern of the Pt(001)/$BaTiO_3$(001)/Pt(001) trilayer. It indicates : Pt[001]//$BaTiO_3$[001]//Pt[001] Pt[100]//$BaTiO_3$[100]//Pt[100].

Pt/$BaTiO_3$/Pt on the top of the MgO substrate. The Pt(202) was chosen for both top and bottom Pt films pole figure measurements, which are shown in Fig. 3b. The sharpness and good symmetry of the diffraction peaks indicate good in-plane alignment between the bottom Pt film and the substrate and between the bottom and the top Pt layers. The pole figure measurement of the $BaTiO_3$ (101) peak in Fig. 3c shows a very good peak distrubution, which indicates a good epitaxial heterostructure of the trilayer. The peak width of $BaTiO_3$ (101) is wider than the Pt (202) peak, which is consistent with the rocking curve measurement.

MICROSTRUCTURE

Transmission electron microscopy (TEM) was used to identify the quality of the epitaxial growth relationship. TEM studies were performed at 300 kV using a Philips CM30 analytical electron microscope with image resolution of 0.23 nm. Selected area and convergent beam electron diffraction patterns were recorded successfully from the substrate and the film in order to determine the relative orientation of the two adjacent layers. An accuracy of better than 0.2° was achieved. In Fig. 4 the electron diffraction pattern of the Pt film on MgO substrate shows Pt[001]//MgO[001] and Pt[100]//MgO[100], which indicates an excellent epitaxial growth relationship between the Pt film and the MgO substrate. The electron diffraction pattern of the trilayer of Pt/$BaTiO_3$/Pt indicates an epitaxial growth relationship between the Pt and the films (Fig. 5), revealing the epitaxial relationships of Pt[001]//$BaTiO_3$[001]//Pt[001] and Pt[100]//$BaTiO_3$[100]//Pt[100]. Fig. 5 is fully consistent with the pole figure measurements on the trilayer of Pt/$BaTiO_3$/Pt as shown in Fig. 3.

DISCUSSION AND SUMMARY

Molecular beam epitaxy (MBE) is most often used to fabricate epitaxial films and epitaxial multilayers. However, other film growth techniques can also be used, for instance laser ablation, sputtering deposition, and chemical vapor deposition. In this work we have shown the feasibility of making epitaxial films and multilayers using the sputtering technique.

The epitaxial growth of Pt films in on oxidizing environment is compatible with epitaxial growth conditions of ferroelectric and magnetic oxides. The role of oxygen in the epitaxial growth is not yet clear, but it is speculated to be associated with mobile PtO spears on the surface.

There are numerous published papers, concerning the effect of bottom electrodes on the electrical properties of ferroelectric films [2]. While fatigue and failure mechanism of ferroelectric capacitors are not completely understood, film orientation is known to be an important determiner of degradation in the remanent polarization [3]. Polycrystalline Pt bottom electrods may induce early failure during fatigue testing. TEM images of our epitaxial trilayer of Pt(001)/$BaTiO_3$(001)/Pt(001) show an abrupt interface (to be published later) between $BaTiO_3$ and Pt bottom electrode. The grain boundary-free nature of the epitaxial trilayer may provide a method for solving the problem.

In conclusion, we have demonstrated the epitaxial growth of Pt(001) on MgO(001) substrates in an oxidizing environment. We have also demonstrated the growth of epitaxial trilayers of Pt(001)/$BaTiO_3$(001)/Pt(001) on MgO(001) substrates. TEM images reveal a sharp interface between the $BaTiO_3$(001) and bottom Pt(001) electrode, which might be helpful for improving the performance of epitaxial ferroelectric capacitors.

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